Nanomechanical properties of plasma-sprayed HfN coating with and without hot isostatic pressing (HIP) treatment were evaluated using nanoindentation. For HIPed HfN coating, the elastic modulus ($E$) and yield strength increase whereas the hardness ($H$), $H/E$ ratio and fraction of the elastic work decrease. HIPed HfN coating shows a larger pile-up around the indent as compared to as-sprayed HfN. HIPing causes densification and improvement in inter-splat bonding which subsequently lead to increase in nanomechanical properties.

Hafnium nitride is characterized by a high melting point, chemical inertness and relatively good oxidation resistance in extreme environments, and is referred to as ultra-high temperature ceramic (UHTC) [1–3]. Hf-based ceramics are expected to be promising materials for hypersonic flight, reusable orbital vehicles and sharp leading edges on future generations of reentry vehicles due to their high melting points and relatively good oxidation resistance in a propulsion environment [4]. Hafnium nitride has been also investigated for potential applications as hard and wear-resistant coating and diffusion barriers [5]. Fabrication of UHTCs into useful shapes and components is a major challenge due to their ultra-high melting point and brittle behavior. Our previous research has shown that Hf-based ceramics can be successfully synthesized as coatings and near net structures by a vacuum plasma spraying (VPS) technique [6]. In the present study, nanomechanical properties of vacuum plasma sprayed HfN coatings have been evaluated using nanoindentation technique.

Basic elastic–plastic responses of coatings can be characterized through tensile or bending tests [7]. However, it is noted that such methods always require complicated sample fabrication, which is extremely difficult for UHTCs such as HfN [8]. Nanoindentation, which does not require complicated sample preparation, can record load and depth continuously throughout the indentation cycle. The load–depth curves can be then analyzed to determine hardness, elastic modulus and fracture toughness. Therefore, nanoindentation test has been widely used to analyze micromechanical response of brittle ceramic materials.

Commercially available HfN powder (average size: 5 μm) with Hf addition (30 wt.%) was employed as the powder feedstock for synthesizing hafnium nitride cermet coating using vacuum plasma spray. Hf was added to provide improved fracture toughness to HfN ceramic with some compromise in the high temperature properties. The details of the processing can be found elsewhere [6]. To obtain fully dense coating, hot isostatic pressing (HIP) was carried out on as-sprayed HfN coating. HIP treatment was performed at 1500 °C and 170 MPa in nitrogen atmosphere for 2 h. Nanoindentation tests were carried out using Hysitron Triboindenter (Hysitron, Minneapolis, MN) with a diamond Berkovich indenter tip. A matrix of $7 \times 7$ indentations (49 indents) was made, spaced $12 \mu m$ apart, giving an overall area of $72 \mu m \times 72 \mu m$. During nanoindentation of as-sprayed HfN, the load was applied at the rate of 25 μN s$^{-1}$ up to a peak load of 1500 μN, where it was held for 2 s and then unloaded completely at negative rate of 25 μN s$^{-1}$. On the other hand, HIPed HfN coatings experienced a peak load...
of 8000 μN applied at the rate of 25 μN s⁻¹ with a hold

time of 10 s and then unloaded completely at negative rate
of 25 μN s⁻¹. The hardness and elastic modulus were cal-
culated by the Oliver and Pharr method [9].

Typical load–displacement curves of indentations
made on as-sprayed HfN and HIPed HfN samples are
shown in Figure 1. It is seen that the loading–unloading
curves for as-sprayed HfN are serrated (Fig. 1a) whereas
those for HIPed HfN samples are smooth (Fig. 1b). The
serrated loading and unloading curves of the as-sprayed
HfN can be attributed to its porosity (∼8 vol.% and
microcracks throughout the coating. Table 1 shows the
measured elastic modulus and hardness for different
HfN samples. It is observed that the elastic modulus in-
creases and the hardness decreases after HIPing of as-
sprayed HfN samples. The ratio of $H/E$ also decreases
after HIP treatment. Hence, it can be deduced that
HIPed HfN behaves more plastically than as-sprayed
HfN. It is reported that the hardness and elastic modu-
lus of HfN(001) films deposited on MgO(001) by mag-
netron sputtering are 25.2 ± 0.7 and 450 ± 9 GPa,
respectively, [10]. The hardness of chemical vapor
deposited (CVD) HfN multilayer coatings on cemented
carbid cutting tools has been reported as 20.1 GPa [5].

Three-dimensional finite-element simulations of elasto-
plastic indentation elucidated the following [14,15]:

$$C = \frac{P_{\text{max}}}{h_{\text{max}}^2} = M_1 \sigma_{0.29} \left\{ 1 + \frac{\sigma_y}{\sigma_{0.29}} \right\} \left\{ \ln \left( \frac{E}{\sigma_y} \right) + M_2 \right\}$$

(3)

$\sigma_y$ is the yield strength, $\sigma_{0.29}$ is the stress corresponding
to the characteristic plastic strain of 0.29 for the inden-
ted material in uniaxial compression, and $M_1$ is
6.618 and $M_2$ is −0.875 for Berkovich indenter [13].
Suresh et al. [13] proposed $\sigma_{0.29}$ to characterize the unique
plastic strain of 0.29 that separates the innermost plastic
cutting region from the plastic region and elastic region
in the indented zone. The ratio of the residual penetra-
tion depth $h_t$ to the maximum penetration depth $h_{\text{max}}$
is an indicator of the extent of deformation, which can
be expressed as [13,15]:

$$\frac{\sigma_{0.29} - \sigma_y}{0.29E} = 1 - 0.142 \frac{h_t}{h_{\text{max}}} - 0.957 \left( \frac{h_t}{h_{\text{max}}} \right)^2$$

(4)

Based on the above-mentioned equations and infor-
mation provided by load–displacement curves, the values
of $W_e/W_t$, $\sigma_{0.29}$ and $\sigma_y$ for HfN coatings are
estimated and listed in Table 1. It is observed that the

Table 1. Measured elastic modulus and hardness of different HfN samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Elastic modulus (GPa)</th>
<th>Hardness (GPa)</th>
<th>$H/E$</th>
<th>$W_e/W_t$</th>
<th>$\sigma_{0.29}$ (GPa)</th>
<th>$\sigma_y$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-sprayed HfN</td>
<td>225 ± 10</td>
<td>12.8 ± 1.6</td>
<td>0.057</td>
<td>0.36</td>
<td>127.5 ± 4.1</td>
<td>93.8 ± 4.1</td>
</tr>
<tr>
<td>HIPed HfN</td>
<td>282 ± 12</td>
<td>9.13 ± 1.5</td>
<td>0.032</td>
<td>0.33</td>
<td>156.4 ± 5.0</td>
<td>117.5 ± 5.0</td>
</tr>
</tbody>
</table>

Figure 1. Load–displacement curves of indentations made on: (a) as-sprayed HfN and (b) HIPed HfN.
strength ($\sigma_y$ and $\sigma_{0.29}$) of HfN increases after HIP whereas its fraction of elastic work ($W_e/W_t$) decreases. This is attributed to the microstructural changes after HIPing. The lower elastic modulus and strength of as-sprayed HfN as compared to HIPed HfN and sputtered HfN film [10] are also attributed to the microstructure.

Plasma-sprayed coatings are characterized by their layered splat microstructure, which is often encompassed by inter-splat pores, cracks and fine voids, leading to inadequate bond strength between the splats. Figure 4a shows the layered microstructure of the as-sprayed HfN coating with a higher concentration of pores at the interface of each layer. The porosity of as-sprayed HfN was measured to be $\sim 8\,\text{vol.\%}$ using image analysis. Therefore, weak bonding between splats and porosity contribute to the significant decrease in the hardness and elastic modulus of as-sprayed HfN compared with dense material [16]. Figure 4b shows
the cross-sectional microstructure of the HfN sample after HIPing. It shows the change in the plasma-sprayed layered structure (Fig. 4a) to more rounded microstructure with a lower porosity level. The porosity decreases to ~2 vol.% with decreases in the splat interface area, inter-splat pores and voids, which results in an increase in the elastic modulus. Energy-dispersive spectroscopy analysis suggested that the gray color phase (Fig. 4b) is the free hafnium that was added to the powder feedstock. It forms a rounded network, with the porous phase (black shade) trapped inside. The decrease in the hardness of HIPed HfN is the consequence of the formation of a large network of metallic Hf. During HIPing, metallic hafnium finds sufficient time to diffuse and agglomerate as opposed to as-sprayed HfN, where fine Hf particles are entrapped in HfN matrix. Greater pile-up ~60 nm (Fig. 3c) in HIPed HfN is also indicative of metallic characteristics, which are attributed to large islands of free hafnium. Table 1 shows that the yield strength ($\sigma_y$ and $\sigma_{0.29}$) of HIPed HfN also increases.

HIPing treatment results in the elimination of weak inter-splat boundaries, which are often mechanically bonded. The formation of a rounded grain structure creates a metallurgical bond that restrains crack formation and propagation under applied load conditions, subsequently leading to an increase in the yield strength of HIPed HfN.

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